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(54) **Detergent composition for
washing fabrics**

(57) Fabrics can be washed with a wash liquor to which has been added a detergent active material, a water-soluble carbonate material such as sodium carbonate and a carboxylic polymer such as hydrolysed polymaleic anhydride or a hydrolysed copolymer of maleic anhydride, ethyl acrylate and vinyl acetate. The polymer reduces the level of inorganic deposition on the fabrics provided that the initial calcium/carbonate saturation ratio in the liquor is below about 50. Thus the method is particularly suitable for use with water having a hardness below 20° FH, at product dosages below 5 g/l, and/or at temperatures below 60°C. the saturation ratio may also be reduced by including a calcium sequestrant such as NTA in the composition.

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SPECIFICATION

Detergent composition and method for its use

- 5 This invention relates to a method of washing fabrics and to a detergent composition, particularly for fabric washing. In particular, but not exclusively, the invention relates to detergent compositions suitable for washing fabrics in moderately soft water and at low temperatures.

10 Detergent compositions commonly incorporate as major ingredients detergent active compounds together with detergency builders. Conventional detergency builders are commonly inorganic materials, particularly the condensed phosphates, for example sodium tripolyphosphate. It has, however, been suggested that the use of phosphate detergency builders can contribute to eutrophication problems. Alternative detergency builders which have been proposed, for example sodium nitrilotriacetate (NTA) and synthetic polyelectrolyte materials tend to be more expensive or less efficient than the phosphate detergency builders, or otherwise unsatisfactory for one reason or another.

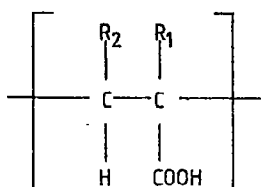
- 25 It is known that sodium carbonate can function as a detergency builder by removing the calcium from hard water in the form of precipitated calcium carbonate. But the calcium carbonate tends to accumulate on washed fabrics, which can lead to fabric harshness and decreased abrasion resistance.

30 British Patent Specification 1 491 978 (Ciba-Geigy) describes a class of polymeric materials based on a maleic anhydride monomer suitable for use as anti-deposition agents in detergent compositions containing phosphate compounds as a detergency builder for the washing of fabrics in relatively hard water.

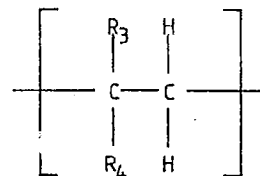
40 We have now surprisingly discovered that a class of polymeric materials such as those described in GB 1 491 978 are unexpectedly useful under certain specified conditions as anti-deposition agents in detergent compositions containing a water-soluble carbonate material as a detergency builder.

45 Thus according to the invention there is provided a method of washing fabrics in water containing calcium hardness, which method comprises adding to said water to form a wash liquor at least

- (i) a synthetic detergent active material;
(ii) a water-soluble carbonate material; and
50 (iii) a polymeric material having an average molecular weight of between about 500 and about 3,000 and having in its molecular structure the group



optionally together with the group



- 55 in which R₁ is hydrogen, or a hydroxyl group; R₂ is hydrogen, an alkyl or alkoxy group having from 1 to 4 carbon atoms, a carboxylic acid group or an acetoxy group; R₃ is hydrogen or an alkyl group having 1 to 4 carbon atoms; and R₄ is hydrogen, a hydroxyl group, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, an aldehyde group, or a carboxylic acid group;

60 the wash liquor having a saturation ratio of the calcium and carbonate present of no more than about 50 and a pH of between about 9.5 and about 11.0.

65 The term "saturation ratio" is well known in the art. See for example A E Nielsen, CEPAS 78, Conference on Electrolytic Precipitation in Aqueous Solution, Panum Institute, University of Copenhagen 1978, 16/18 August. For any composition it may easily be calculated from the following equation:

$$SR = \sqrt{\frac{a_{Ca} \cdot a_{CO_3}}{K_{SO}}}$$

- 75 where SR is the saturation ratio, a_{Ca} is the initial activity of the calcium ions, a_{CO_3} is the initial activity of the carbonate ions and K_{SO} is the thermodynamic solubility product of calcite. The activity of the calcium ions and the carbonate ions depends on their concentration and the ionic strength of the solution, the latter depending on various other components, in particular ionic salts, which may be present in the wash liquor. The following table, Table I, illustrates how the saturation ratio of calcium and carbonate under a number of possible
85 conditions can vary.

TABLE I

	A	B	C	D	E	F
Carbonate ion concentration ($\times 10^{-4}\text{M}$)	60	60	60	60	60	60
Calcium ion concentration ($\times 10^{-4}\text{M}$)	12	12	12	12	12	12
Sodium sulphate concentration ($\times 10^{-4}\text{M}$)	48	168	288	48	48	48
Temperature $^{\circ}\text{C}$	40	40	40	25	60	90
Saturation ratio	28.0	22.6	19.8	20.7	40.1	64.0

It is clear from Table I that the factors which contribute to a lowering of the saturation ratio include lower temperatures and increased ionic strength. It is clear also that the saturation ratio is lower when the carbonate ion concentration is lower and the calcium ion concentration is lower.

It is an essential feature of the present invention that the saturation ratio be below about 50.0, preferably below about 40.0, most preferably below about 35.0.

Thus, it is a preferred feature of the method according to the invention, that the wash liquor in contact with the fabrics has a maximum temperature of about 60°C , most preferably not more than about 50°C .

Also, it is a preferred feature of the method according to the invention that the wash liquor is formed by adding to the water a detergent composition at a dosage level of not more than about 5g composition per litre, most preferably not more than about 4g per litre.

Further, it is a preferred feature of the method according to the invention that the water used to form the wash liquor has a calcium hardness of not more than about $2.0 \times 10^{-3}\text{M}$ calcium ions/litre, most preferably not more than about $1.5 \times 10^{-3}\text{M}$.

However, additional sequestrants may be used in harder water to lower the saturation ratio to below the preferred value. This is demonstrated below for the trisodium salt of nitrilotriacetic acid which, to a good approximation, can be assumed to interact with calcium under the conditions herein on a 1:1 molar basis.

Example A in Table I shows the conditions that would pertain in a wash solution when a product containing 31.8% sodium carbonate and 34.1% sodium sulphate is used at 2.0 g/l product concentration in $1.2 \times 10^{-3}\text{M}$ Ca water. In the table below, Table II, the value for the saturation ratio for the same "product" in $2.4 \times 10^{-3}\text{M}$ Ca water is shown for 40°C along with the SR values for the replacement of sodium sulphate by 5%, 10% and 15% NTA.

TABLE II

	A	G	H	I	J	K
Sodium carbonate/ $\text{M} \times 10^{-4}$	60	60	60	60	60	90
Calcium Chloride/ $\text{M} \times 10^{-4}$	12	24	24	24	24	24
Sodium sulphate/ $\text{M} \times 10^{-4}$	48	48	41.0	33.9	26.9	0
Trisodium nitrilo- triacetate/ $\text{M} \times 10^{-4}$	0	0	3.89	7.78	11.7	11.7
Saturation ratio	28.0	38.5	35.2	31.5	27.4	33.4

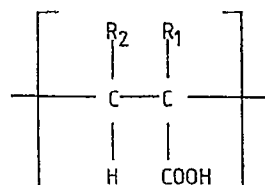
It is clear from Table II that for $2.4 \times 10^{-3}\text{M}$ Ca water and medium carbonate level (31.8%) NTA is desirable to reduce the saturation ratio to below 35 and about 10% NTA is sufficient. For a higher carbonate level (Example K, 47.7% carbonate) about 15% NTA would be required.

These features can clearly be traded off against one another. Thus, for examples, higher dosage levels are satisfactory at particularly low water hardness levels while at lower temperatures higher dosage levels and a higher water hardness can be tolerated.

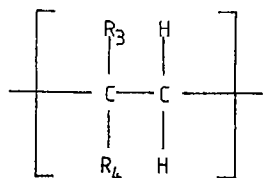
Also according to the invention there is provided a detergent composition for washing fabrics, the composition containing:

- (i) from about 5% to about 40% by weight of a synthetic detergent active material;
- (ii) from about 10% to about 70% by weight of a water-soluble carbonate material; and

- (iii) from about 0.05% to about 5% by weight of a polymeric material having an average molecular weight of between about 500 and about 3,000 and having in its molecular structure the group



optionally together with the group



in which R₁ is hydrogen, or a hydroxyl group; R₂ is hydrogen, an alkyl or alkoxy group having from 1 to 4 carbon atoms, a carboxylic acid group or an acetoxy group; R₃ is hydrogen or an alkyl group having 1 to 4 carbon atoms; and R₄ is hydrogen, a hydroxyl group, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, an aldehyde group, or a carboxylic acid group;

- 5 the composition when added to water containing calcium hardness at a level 1.2×10^{-3} M calcium ions, at a dosage of 1g composition per litre and at a temperature of 20°C yielding a saturation ratio of the calcium and carbonate present of no more than
10 about 50 and a pH of between about 9.5 and about 11.0.

- The detergent active compounds used in the compositions of the invention may be any of the conventional anionic, nonionic, amphoteric or zwitterionic detergent active compounds and mixtures thereof, but preferably they do not form excessively water-insoluble calcium salts in hard water during use. Many such detergent active compounds are commercially available and are fully described in the literature, for example in "surface Active Agents and Detergents", Vols I and II, by Schwartz, Perry & Berch. Preferred suitable detergent active compounds which can be used include nonionic detergent active compounds which cannot of course form calcium salts, and anionic detergent active compounds which form water-soluble calcium salts, as for example alkyl ether sulphates, or which form insoluble calcium salts when used alone but are used in conjunction with additional solubilising compounds, particularly other detergent active compounds, for example mixtures of sodium alkyl benzene sulphonates with nonionic detergent active compounds and some mixed olefin sulphonates, wherein some of the olefin sulphonate constituents appear to act as solubilising agents for the other less-soluble constituents.

- Specific nonionic detergent active compounds which can be used in the compositions of the invention include ethoxylated fatty alcohols, preferably linear nonhydric alcohols with C₁₀-C₁₈, preferably C₁₀-C₁₅, alkyl groups and about 5-15, preferably 7-12, ethylene oxide (EO) units per molecule and ethoxylated alkylphenols with C₈-C₁₆ alkyl groups preferably C₈-C₉ alkyl groups, and from about 4-12 EO units per molecule. The nonionic compounds are often used in admixture with minor amounts of other detergent-active compounds especially anionic compounds, to improve lather characteristics and powder properties. Mixtures of nonionic compounds with amine oxide can also give good results.

The preferred anionic detergent active compound

which forms soluble or only slightly insoluble calcium salts are alkyl (C₁₀-C₂₀) sulphates and alkyl ether (1-20 EO) sulphates, particularly those with C₁₀-C₁₅ alkyl groups and 1-7 EO, and olefin sulphate detergent active compounds obtained when the products of the sulphonation of olefins are neutralised and hydrolysed. The olefins used are preferably linear C₁₂-C₂₀ alpha olefins particularly C₁₄-C₁₆ alpha olefins, produced for example by the "cracked-wax" process, or by the "Zeigler" process, but localised internal, random or so-called vinylidene olefins may alternatively be used. The anionic detergent active compounds are used in the form of the alkali metal, ammonium or substituted ammonium salts, preferably the sodium salts.

- Other detergent active compounds which do not form insoluble calcium salts, but which are of less commercial interest, include salts of esters of alpha sulphonated (C₁₀-C₂₀) fatty acids with C₁-C₁₀ alcohols, preferably C₁-C₃ alcohols; salts of 2 - acyloxalkane - 1 - sulphonic acids, particularly wherein the alkyl group contains from about 10-22, preferably 12-16, carbon atoms, and the ester forming group contains from 1-8 carbon atoms; trialkyl amine oxides having a C₁₀-C₂₂ alkyl group, and two C₁-C₄ alkyl or C₂-C₃ hydroxyalkyl groups; and dialkyl sulfoxides having a C₁₀-C₂₂ alkyl group and a C₁-C₄ alkyl or C₂-C₃ hydroxy alkyl group, together with detergent active betaines and sulphobetaines.

- As stated earlier, mixtures of some detergent active compounds can give particularly good results. Specifically alkyl benzene sulphonates (which when used alone tend to form insoluble calcium salts) can be used with minor amounts of certain solubilising compounds, such as nonionic, alkyl sulphate or alkyl ether sulphate detergent active compounds, to give good detergent properties and be relatively economical. The ratio by weight of such solubilising compounds to the alkyl benzene sulphonate is preferably from 1:1 to 1:10, especially from 1:2 to 1:8. Further, while the detergent active material would not generally be wholly soap, soap may be present with other detergent active compounds, as for example in binary or ternary mixtures.

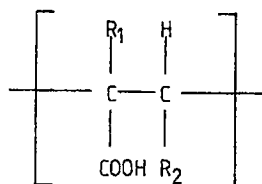
- The amount of the detergent active compound or compounds is generally in the range of from 5 to 40 per cent, preferably from 5 to 30 per cent by weight in the composition. Suitable amounts of detergent active compound are usually in excess of 8% by weight.

- The water-soluble carbonate material used is preferably an alkali metal carbonate such as sodium or potassium carbonate or a mixture thereof, for reasons of cost and efficiency. The carbonate salt may be wholly or partially neutralised, for example a sesqui-carbonate may be used in partial replacement of the carbonate salt. The amount of the alkali metal carbonate in the detergent composition can be varied widely but the amount is desirably at least about 20% by weight, preferably from 35 to 65% by weight. The amount of the carbonate detergency builder can approach about 70% by weight, whilst still leaving room for the anti-deposition agent and detergent active compound or compounds. It should be mentioned within this range the higher levels

tend to be required under conditions of use at low product concentration, as is usually the practice in North America, and the converse applies at higher product concentrations as tend to be used in Europe.

- 5 It may also be desirable to limit the carbonate content to a lower figure to decrease the risk of internal damage following any accidental oral ingestion.

The polymeric anti-deposition agent is a polycarboxylate material. One group of polycarboxylate materials found to be of value in the present invention comprises homopolymers having a repeating unit of formula



where R_1 is H, OH, C_1 - C_4 alkyl or alkoxy or acetoxy, R_2 is H or $-COOH$.

This group of polycarboxylates include polyacrylic, polymethacrylic, polyitaconic, polymaleic and polyhydroxyacrylic acids, and also the hydrolysis products of the corresponding polymerised acid anhydrides.

Polymeric maleic anhydride is essentially a homopolymer of maleic anhydride and may be hydrolysed very readily, for example, by heating with water, to form a polymeric product which contains free carboxylic acid groups, and possibly some residual anhydride groups, on a carbon backbone; the product is not pure polymaleic acid. The actual structure of the product is not known and so this type of polymeric product formed by hydrolysing polymaleic anhydride will be referred to in this specification as "hydrolysed polymaleic anhydride".

A second group of polycarboxylate materials comprises copolymers of maleic acid with an olefinic monomer such as ethylene, or vinyl methyl ether.

The ratio of the number of units of maleic acid to those of the other monomer should preferably be in the range from 1:1 to 3:1.

The polycarboxylate materials are preferably used in the form of their alkali metal, especially sodium salts, and the level of usage of these polycarboxylate materials, calculated as the sodium salts, in the compositions of the invention is from 0.1% to 5.0% by weight of the composition, preferably from 0.5% to 5% and most preferably from 1.0% to 3% by weight.

These materials may also be the hydrolysed copolymer of maleic anhydride and an ethylenically unsaturated co-monomer. The ethylenically unsaturated monomers for copolymerisation with maleic anhydride may be selected from a wide range of materials, for example, acrylic acid, methacrylic acid, crotonic acid, itaconic acid or its anhydride, acotinic acid (and their esters) eg ethyl acrylate and methacrylate, acrylonitrile, acrylamide, vinyl acetate; styrene; α -methyl styrene; methyl vinyl ketone; acrolein; ethylene; propylene; or mixtures thereof.

When mixtures of monomers are used, the resulting polymer may be, eg, a terpolymer such as that derived from maleic anhydride and two other monomers, eg, vinyl acetate and ethyl acrylate.

Particularly preferred copolymers are those derived from hydrolysed copolymers of maleic anhydride and acrylic acid, its amide and its esters, methacrylic acid, its amide and its esters, and vinyl esters.

Further details of these polymers and methods of preparing them are disclosed in British Patent Specifications 1 369 429, 1 411 063, 1 414 918 and 1 491 978 whose disclosures are incorporated herein by reference.

While the presence of a calcium sequestrant in the compositions according to the invention is not essential, compositions may further comprise from about 5% to about 20% by weight of a calcium sequestrant having a calcium ion sequestering capacity sufficient to decrease the concentration of free calcium ions in solution containing $1.2 \times 10^{-3}M$ of calcium ions to a concentration of not more than about $2.0 \times 10^{-4}M$ when the sequestrant is employed in an amount of 0.1% by weight of the solution.

The level of calcium ions in an aqueous solution can be determined using a calcium specific electrode which develops a potential across a thin layer of water-insoluble ion-exchange liquid which is held rigidly by an inert porous membrane disc. The liquid is a calcium salt of an organic phosphoric acid which exhibits very high specificity for calcium ions. An internal solution of calcium chloride contacts the inside surface of the membrane disc to provide a stable potential between the internal reference electrode and the ion-exchange liquid layer. In use, the calcium-specific electrode is immersed in a solution containing $1.2 \times 10^{-3}M$ of calcium ions and a solution of the sequestering agent under test is added in increments over 1 hour at 25°C. The potential generated is determined and related to that of standard solutions to find the calcium ion concentration in the presence of 0.1% of the sequestrant under test.

Many suitable sequestering agents are known and are commercially available. Examples of suitable sequestering agents include the water-soluble salts of aliphatic hydroxy-polycarboxylic acid sequestrants such as citric acid, cyclic aliphatic and aromatic polycarboxylic acids such as cyclopentane tetracarboxylic acid and mellitic acid, and salts of polycarboxylic acids containing ether links, such as oxydiacetic acid, oxydisuccinic acid and carboxymethyloxysuccinic acid and the polyacetal carboxylates described in US 4 144 126 and US 4 146 495, and homologues and analogues of these compounds, and sodium nitrilotriacetate. Mixtures of two or more of these suitable sequestering agents may be used if desired, for example because of supply or biological problems. It will be appreciated that these compounds are usually used in water-soluble or dispersible salt form, particularly as the alkali metal, for example sodium, salts or as the ammonium or substituted ammonium salts, but it may be possible to use the sequestrants in acid form

for neutralisation in solution. The sequestering agent is conveniently sodium citrate which is commercially available and biologically acceptable. The amount of the sequestering agent which is used should be from 5 to 20%, by weight of the composition, preferably from about 10 to about 20% by weight. The maximum level of the sequestering agent is dictated by practical considerations, particularly the cost of the sequestering agent in relation to other ingredients. Most preferably, the sequestering agent is present at a level less than the level of the water-soluble carbonate material.

In addition to the essential carbonate compound, and the anti-deposition agent, it is possible to include minor amounts of other detergency builders (ie at levels less than the level of the water-soluble carbonate material), provided that the total amount of the detergency builders does not exceed about 85% by weight, so as to leave room in the compositions for other essential ingredients. One such optional ingredient which has a detergency building effect is an alkali metal silicate, particularly sodium silicate, for example sodium alkaline or metasilicate. A low level of silicate, for example about 5 - 10% by weight, is usually advantageous in decreasing the corrosion of metal parts in fabric washing machines and may give process benefits, as well as assisting to control the pH of the composition which should be about 9.5 to 11, preferably about 10.0 to 10.6 for a wash solution at the desired product concentration. If higher levels of silicate are used, there can be a noticeable improvement in detergency, which may permit some decrease in the alkali metal carbonate content.

Other detergency builders which can be present in minor amounts, include particularly other so-called precipitant builders which form insoluble calcium salts, for example sodium salts of long-chain alpha-sulphonated monocarboxylic acids and sodium alkyl and alkenyl succinates and malonates and analogous compounds. It will be appreciated that some of these materials contain phosphorus which may detract from their usefulness in any compositions specifically intended to have a low level of phosphorus, or none at all. Ion-exchange detergency builders such as the various sodium aluminosilicates disclosed in the literature may also be present.

Apart from the detergent active compounds and detergency builders, detergent compositions according to the invention can contain any of the conventional fabric-washing detergent composition additives in the amounts in which such additives are normally employed in fabric-washing detergent compositions. Examples of these additives included lather boosters such as alkanolamides, particularly ethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, anti-redeposition agents such as sodium carboxymethylcellulose, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, per-acid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes, germicides and col-

ourants.

The detergent compositions of the invention may be produced by any of the techniques commonly employed in the manufacture of fabric-washing detergent compositions, including particularly slurry-making and spray-drying processes, where the whole composition may usually be spray dried unless bleaching agents are present, and the compositions may be prepared in any of the common physical forms associated with fabric-washing detergent compositions, such as powders, granules, cakes and liquids.

The invention will now be illustrated by the following non-limiting examples, in which all parts and percentages are by weight unless otherwise specified. The percentage levels of components listed in the following examples are quoted as if the anhydrous materials had been used. In practice, the commonly available hydrates were used and the water of crystallisation of these materials is listed together with any other water present in the compositions.

EXAMPLES 1 TO 3

Detergent compositions were prepared according to Table III below. Each composition was used to wash cotton poplin fabrics in a Tergotometer apparatus under the conditions stated. After 15 washes, the percentage inorganic deposition on the fabrics was determined by combustion, and is recorded in Table III as "% Ash(15)".

TABLE III

EXAMPLE:	1	2	3
<i>Composition</i>			
Nonionic detergent active ¹	10%	10%	10%
Sodium carbonate	35%	35%	35%
Sodium alkaline silicate	10%	10%	10%
Sodium sulphate	40%	40%	40%
Polymer - B ²	2%	—	—
Polymer - T ³	—	2%	—
Water & minor ingredients	—balance to 100—		
Temperature °C	40	40	40
Dosage g/l	2	2	2
Liquor: fabric ratio	1:300	1:300	1:300
Hardness °F (Ca)	12	12	12
Hardness °F (Mg)	6	6	6
pH	10.4	10.4	10.4
Saturation ratio (approx)	30	30	30
% Ash (15)	1.6	2.2	5.4

1. Neodol 45-13EO obtained from Shell Chemical Company.
2. Belgard EV - hydrolysed polymeric maleic anhydride having an average molecular weight of about 1000.
3. Hydrolysed copolymer of maleic anhydride, ethyl acrylate and vinyl acetate made in accordance with Example 1 of GB 1 491 978.

Examples 1 and 2 demonstrate that the level of inorganic deposition on fabrics is lower when the compositions contain the polymeric materials according to the invention in comparison with the identical composition containing no polymer.

EXAMPLES 4 TO 6

By way of comparison the procedure of Examples 1 to 3 was repeated under conditions of higher saturation ratio. The compositions used, conditions 5 and results are set out in the following Table IV.

TABLE IV

EXAMPLE	4	5	6
10 Composition			
Anionic detergent active ⁴	20	20	20
Sodium carbonate	35	35	35
Sodium alkaline silicate	10	10	10
Sodium sulphate	11	11	13
15 Sodium perborate	20	20	20
Polymer - B	2	—	—
Polymer - T	—	2	—
Water & minor ingredients	— balance to 100 —		
Temperature °C	60	60	60
20 Dosage g/l	5	5	5
Liquor to fabric ratio	1:300	1:300	1:300
Hardness °F (Ca)	30	30	30
pH	10.4	10.4	10.4
Saturation ratio (approx)	85	85	85
25 % Ash (15)	7.0	6.4	2.1

4. Dodecyl benzene sulphonate.

Examples 4, 5 and 6 demonstrate that where the 30 saturation level is high, the level of inorganic deposition saturation level is high, the level of inorganic deposition on fabrics is higher when the compositions contain the polymeric materials according to the invention than when the composition contains no polymer.

EXAMPLES 7 AND 8

Examples 7 and 8 are the results of experiments conducted in washing machines (Kenmore machines, ex USA). The compositions used, conditions and results are set out in the following Table V.

TABLE V

Example	7	8
45 Nonionic detergent active ⁵	10	10
Sodium carbonate	35	35
Sodium silicate	10	10
Sodium sulphate	40	40
Polymer B	—	1
50 Temperature °C	40	40
Dosage g/l	2	2
Liquor to fabric ratio	1:20	1:20
Hardness °FH (2Ca/Mg)	12/6	12/6
pH	10.4	10.4
55 Saturation ratio (approximately)	28	28
% Ash (20 washes) Cotton	3.2	2.4
Polyester cotton	3.0	1.3

5-Neodol 45.13EO

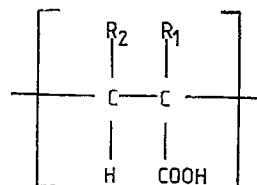
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Examples 7 and 8 show that when the compositions contain the low molecular weight polymers according to the invention lower ash levels arise than when the composition contains no polymer.

65 CLAIMS

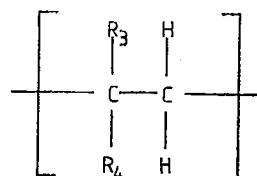
1. A method of washing fabrics in water containing calcium hardness, which method comprises adding to said water to form a wash liquor at least

- (i) a synthetic detergent active material;
 70 (ii) a water-soluble carbonate material; and
 (iii) a polymeric material having an average molecular weight of between about 500 and about 3,000 and having in its molecular structure the group



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optionally together with the group



in which R₁ is hydrogen, or a hydroxyl group; R₂ is hydrogen, an alkyl or alkenyl group having from 1 to 4 carbon atoms, a carboxylic acid group or an acetoxy group; R₃ is hydrogen or an alkyl group having 1 to 4 carbon atoms; and R₄ is hydrogen, a hydroxyl group, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, an aldehyde or a carboxylic acid group;

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85 the wash liquor having a saturation ratio of the calcium and carbonate present of no more than about 50 and a pH of between about 9.5 and about 11.0.

2. A method in accordance with Claim 1, wherein 90 the maximum temperature of the wash liquor in contact with the fabrics is about 60°C.

3. A method in accordance with Claim 1, wherein the wash liquor is formed by adding to the water a detergent composition at a dosage level of not more 95 than about 5g composition per litre.

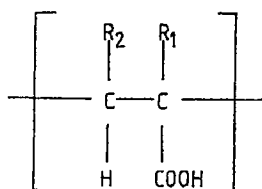
4. A method in accordance with Claim 1, wherein the water contains calcium hardness at a level of not more than about 2.0×10^{-3} M calcium ions/litre.

5. A method in accordance with Claim 1, including 100 additionally adding to said water, a calcium sequestrant as hereinbefore defined.

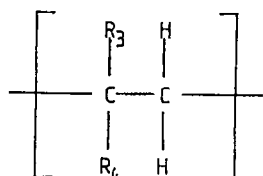
6. A detergent composition for washing fabrics in accordance with the method of Claim 1, the composition containing:

- 105 (i) from about 5% to about 40% by weight of a synthetic detergent active material;
 (ii) from about 10% to about 70% by weight of a water-soluble carbonate material; and
 (iii) from about 0.05% to about 5% by weight of a polymeric material having an average molecular weight of between about 500 and about 3,000 and having in its molecular structure the group

110



optionally together with the group



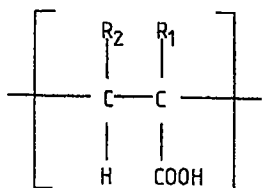
- 5 in which R_1 is hydrogen, or a hydroxyl group;
 R_2 is hydrogen, an alkyl or alkoxy group
 having from 1 to 4 carbon atoms, a carboxylic
 acid group or an acetoxy group; R_3 is hyd-
 10 rogen or an alkyl group having 1 to 4 carbon
 atoms; and R_4 is hydrogen, a hydroxyl group,
 an alkyl group having 1 to 4 carbon atoms, an
 alkoxy group having 1 to 4 carbon atoms, an
 15 aldehyde group, or a carboxylic acid group;
 the composition when added to water containing
 calcium hardness at a level $1.2 \times 10^{-3}M$ calcium ions,
 at a dosage of 1g composition per litre and at a
 temperature of $20^\circ C$ yielding a saturation ratio of the
 calcium and carbonate present of no more than
 about 50 and a pH of between about 9.5 and about
 11.0.

7. A composition according to Claim 6, addi-
 20 tionally containing from about 5% to about 20% of a
 calcium sequestrant as hereinbefore defined.

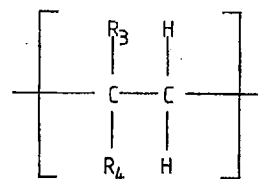
New claims or amendments to claims filed on 11th
 January 1983

Superseded claims 1-7

- 25 1. A method of washing fabrics in water contain-
 ing calcium hardness, which method comprises
 adding to said water to form a wash liquor at least
 30 (i) a synthetic detergent active material;
 (ii) a water-soluble carbonate material; and
 (iii) a polymeric material having an average
 molecular weight of between about 500 and
 about 3,000 and having in its molecular struc-
 ture the group



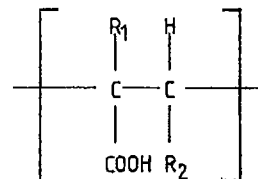
- 35 optionally together with the group



- 40 in which R_1 is hydrogen, or a hydroxyl group;
 R_2 is hydrogen, an alkyl or alkoxy group
 having from 1 to 4 carbon atoms, a carboxylic
 acid group or an acetoxy group; R_3 is hyd-
 rogen or an alkyl group having 1 to 4 carbon
 atoms; and R_4 is hydrogen, a hydroxyl group,
 an alkyl group having 1 to 4 carbon atoms, an
 alkoxy group having 1 to 4 carbon atoms, an
 aldehyde or a carboxylic acid group;

- 45 the wash liquor having a saturation ratio of the
 calcium and carbonate present of no more than
 about 50 and a pH of between about 9.5 and about
 11.0.

2. A method of washing fabrics in water contain-
 50 ing calcium hardness, which method comprises
 adding to said water to form a wash liquor at least
 (i) a synthetic detergent active material;
 (ii) a water-soluble carbonate material; and
 (iii) a polymeric material having an average
 55 molecular weight of between about 500 and
 about 3,000 and having in its molecular
 structure the group



where R_1 is H, OH, C_1 - C_4 alkyl or alkoxy or
 acetoxy, R_2 is H or $-COOH$,

- 60 the wash liquor having a saturation ratio of the
 calcium and carbonate present of no more than
 about 50 and a pH of between about 9.5 and about
 11.0.

3. A method in accordance with Claim 1 or 2,
 65 wherein the maximum temperature of the wash
 liquor in contact with the fabrics is about $60^\circ C$.

4. A method in accordance with Claim 1 or 2,
 wherein the wash liquor is formed by adding to the
 water a detergent composition at a dosage level of
 70 not more than about 5g composition per litre.

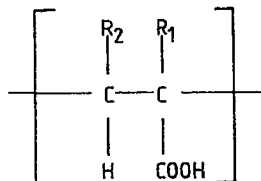
5. A method in accordance with Claim 1 or 2,
 wherein the water contains calcium hardness at a
 level of not more than about $2.0 \times 10^{-3}M$ calcium
 ions/litre.

- 75 6. A method in accordance with Claim 1 or 2,
 including additionally adding to said water, a cal-
 cium sequestrant as hereinbefore defined.

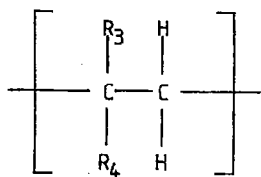
7. A detergent composition for washing fabrics
 in accordance with the method of Claim 1, the
 80 composition containing:

- (i) from about 5% to about 40% by weight of a
 synthetic detergent active material;
 (ii) from about 10% to about 70% by weight of a
 water-soluble carbonate material; and

- (iii) from about 0.05% to about 5% by weight of a polymeric material having an average molecular weight of between about 500 and about 3,000 and having in its molecular structure the group



optionally together with the group



in which R₁ is hydrogen, or a hydroxyl group; R₂ is hydrogen, an alkyl or alkoxy group having from 1 to 4 carbon atoms, a carboxylic acid group or an acetoxy group; R₃ is hydrogen or an alkyl group having 1 to 4 carbon atoms; and R₄ is hydrogen, a hydroxyl group, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, an aldehyde or a carboxylic acid group;

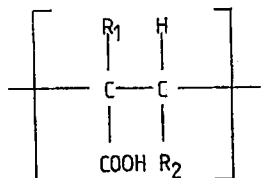
the composition when added to water containing calcium hardness at a level $1.2 \times 10^{-3} \text{M}$ calcium ions, at a dosage of 1g composition per litre and at a temperature of 20°C yielding a saturation ratio of

the calcium and carbonate present of no more than about 50 and a pH of between about 9.5 and about 11.0

8. A detergent composition for washing fabrics in accordance with the method of Claim 2, the

composition containing:

- (i) from about 5% to about 40% by weight of a synthetic detergent active material;
- (ii) from about 10% to about 70% by weight of a water-soluble carbonate material; and
- (iii) from about 0.05% to about 5% by weight of a polymeric material having an average molecular weight of between about 500 and about 3,000 and having in its molecular structure the group



where R₁ is H, OH, C₁-C₄ alkyl or alkoxy or acetoxy, R₂ is H or -COOH,

the composition when added to water containing calcium hardness at a level $1.2 \times 10^{-3} \text{M}$ calcium ions, at a dosage of 1g composition per litre and at a

temperature of 20°C yielding a saturation ratio of the

calcium and carbonate present of no more than about 50 and a pH of between about 9.5 and about 11.0.

9. A composition according to Claim 7 or 8 additionally containing from about 5% to about 20% of a calcium sequestrant as hereinbefore defined.

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